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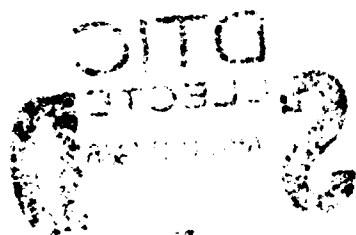
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was developed to determine, separately, the faradaic and charging components of the polarographic current, based on the different time-dependencies of these two components. Condensed thymine monolayers inhibit many electrode reactions. With these monolayers the surface pressure can be varied (by varying the bulk thymine concentration) without changing the composition of the film or its charge density. Research completed on thymine provides a uniquely thorough and comprehensive account of the thermodynamics and kinetics of film formation, a subject of considerable practical importance in corrosion protection. Developed were a number of novel ideas and new experimental approaches. FINAL REPORT, Electrosorption of Organic Molecules, AFOSR-84-0017.



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This report covers the period from October 1, 1983 through September 30, 1985. During this period, a number of significant results were obtained, which are described below.

1. Interfacial tension measurements

We have used the maximum bubble pressure method to measure the interfacial tension of the mercury-solution interface in the presence of thymine. This particular adsorbate was selected because it can form, over a range of concentrations and potentials, a condensed film at the mercury-water interface. The measurements have been completed and a manuscript is in preparation. The results of this study can be summarized as follows:

a. The condensed film has a constant composition, independent of either potential or bulk thymine concentration, corresponding with a surface excess of 3.9 micromoles per square meter.

b. This particular value of the surface excess suggests that the molecular organization in the condensed film is like that of thymine in its anhydrous crystal [1] or in its 1:1 complex with p-benzoquinone [2]. In these crystals, thymine molecules are arranged in planar layers which contain "ribbons" in which each thymine molecule is linked by double hydrogen-bonds to two of its neighbors, see Fig. 1. These crystal planes exhibit, within experimental error, the same density (of $3.8 \mu\text{moles m}^{-2}$).

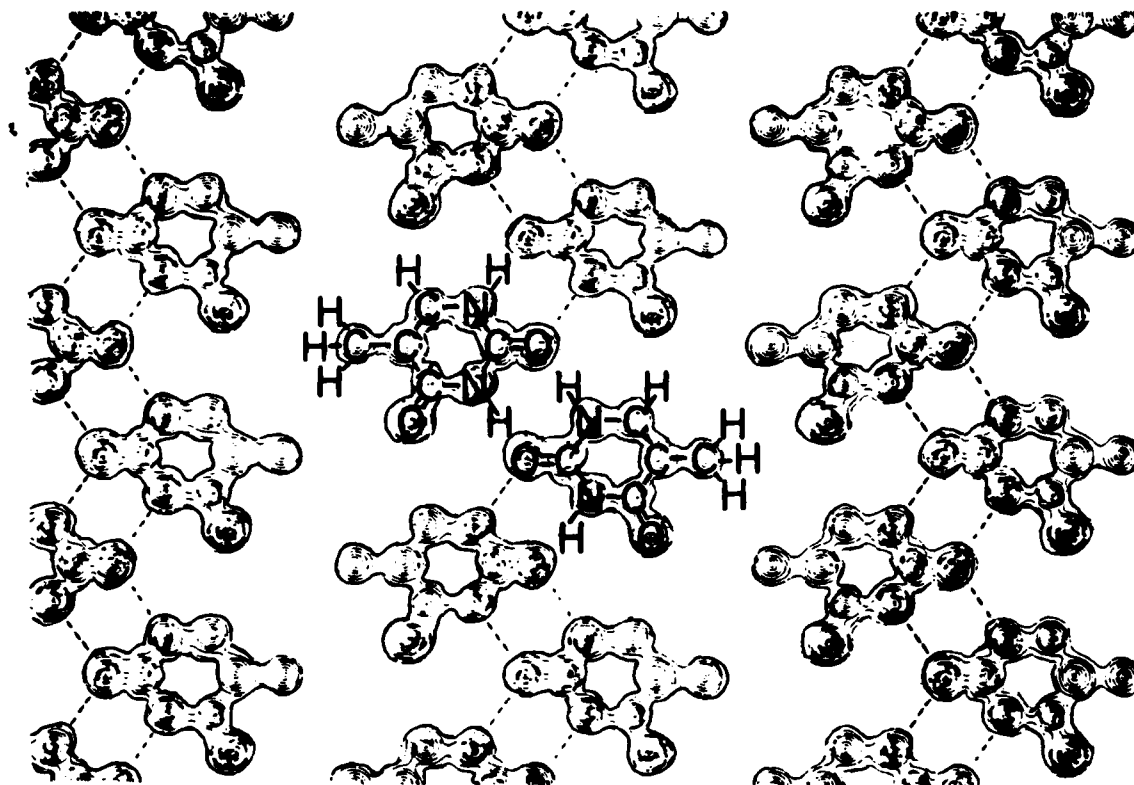


Fig. 1. The arrangement of thymine in anhydrous thymine crystals [1], in which it forms planar ribbons of hydrogen-bonded molecules with a density of $38 \mu\text{moles m}^{-2}$, within experimental error the same density as observed for the condensed two-dimensional thymine film, see Fig. 2. The chemical structure has been superimposed on two molecules in the electron density map; dotted lines indicate hydrogen bonds.

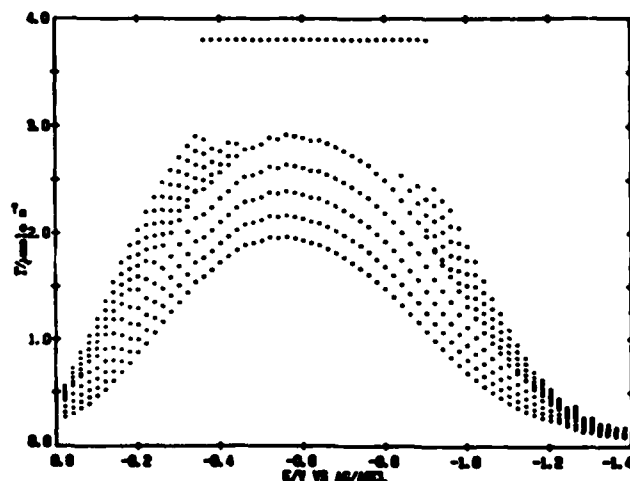


Fig. 2. The surface excess of thymine in aqueous 1.0 M NaCl as a function of potential (vs. Ag/AgCl) and thymine concentration (ranging from 5.0 to 24.7 mM), at 25°C, as determined from our maximum bubble pressure measurements of interfacial tension.

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c. Such double hydrogen bonding makes it possible to understand the formation of a condensed monolayer film at the mercury-water interface, which can only be stable when the adsorption of the organic molecules to the metal is combined with strong adsorbate-adsorbate interactions. To our knowledge, this is the first time that interfacial tension measurements have provided evidence for a specific molecular arrangement; the usual comparison with molecular models based on Van der Waals radii [3] leads to much lower packing densities and, therefore, cannot explain our experimental results.

d. The values for the surface excess obtained from our measurements, see Fig. 2, indicate that the transition between normal (two-dimensional gas-like) adsorption and that in the condensed film involves a critical surface excess, of about 2.6 to 2.9 $\mu\text{moles m}^{-2}$, in accordance with earlier theoretical predictions [4]. The slight variation of this limiting surface excess with potential, see Fig. 2, is most likely due to potential-dependent chloride specific adsorption before film formation.

2. Capacitance measurements

We have completed our capacitance measurements on this same system; a manuscript describing our results is in press [5] and is attached as appendix 1. These measurements are in full agreement with the interfacial tension data and, incidentally, are much easier to obtain. Capacitance measurements are often used as a convenient substitute for interfacial tension data. However, the present case illustrates that such a substitution is not

always feasible. The capacitance "pit" has very sharp and narrow desorption-adsorption peaks at its edges, which can be observed only at low frequencies and which cannot be measured with sufficient precision; without these, integration of the capacitance leads to physically absurd conclusions.

We have also used voltage step measurements to obtain the initial capacitance values in the pit region, i.e., the capacitance obtained immediately after a voltage step, before the condensed film has had time to nucleate and grow. These data can be integrated to provide the corresponding, "virtual" interfacial tension data. Comparison between the virtual and actual interfacial tensions yields the change in interfacial tension during film condensation, i.e., the thermodynamic driving force for film growth. Fig. 3 illustrates this type of capacitance data. A manuscript describing our method (which is novel) and its results is in preparation.

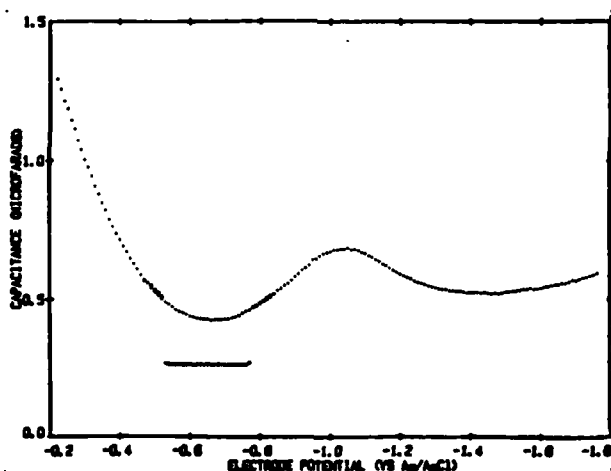


Fig. 3. The initial capacitance measured immediately after a voltage step, and its steady-state value, measured on single mercury drops in 1 M NaCl + 14 mM thymine at 25°C with a measurement frequency of 1.19 KHz.

3. Charge density measurements

We have developed a simple method to determine, separately, the faradaic and charging components of the polarographic current, based on the different time-dependencies of these two components [6]. This method may have analytical usefulness. We have subsequently applied it to the direct measurement of the charge density of thymine adsorbed at the mercury-water interface. The data so obtained are, also, in complete quantitative agreement with the interfacial tension results. Fig. 4 illustrates some of our experimental results; a manuscript describing these observations is in preparation. The most interesting conclusion from these measurements is that they show, directly and unambiguously, that the condensed film has a potential of zero charge which is quite different from that obtained in the presence of "normal" thymine adsorption.

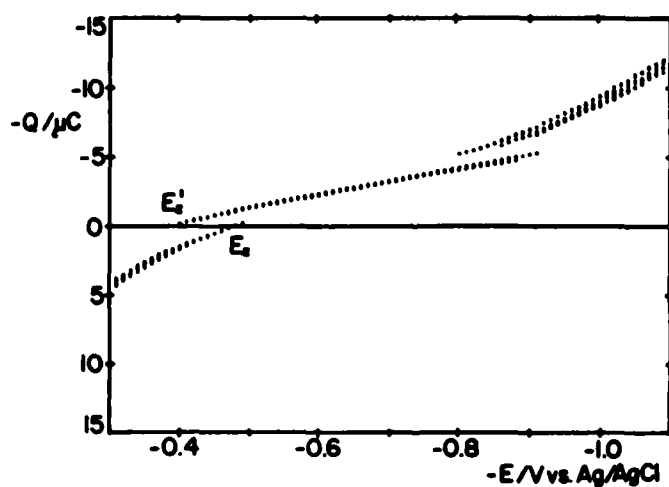


Fig. 4. The electrode charge measured directly on a dropping mercury electrode, using the method of reference [6], for 15.0, 16.6, 18.3, 20.2, 22.4 and 24.7 mM thymine in 1 M NaCl at 25°C. Note the different potentials of zero charge, E_z and E_z' .

4. Nucleation kinetics

The study of the kinetics of formation of condensed thymine films is the only area of research where we have not yet obtained completely satisfactory experimental results. The problem can be identified, but its solution has proven to be rather elusive. The difficulty stems from the use of a very small electrode surface, necessary for the observation of individual nucleation events [7]. On a larger electrode surface, deterministic rather than stochastic results are obtained. The deterministic results, such as described in [5], do not allow the separate determination of the nucleation and growth rate parameters.

Our small electrodes have an unfavorable ratio of area to periphery. Although most nucleations occur at the mercury-water interface, a small percentage of them appear to happen in the three-phase region where the mercury, water and capillary glass meet. The problem only shows up in the statistical data analysis, and can be remedied by using a capillary soaked extensively in water. However, after several hours, such capillaries begin to give contact problems due to breakage of the mercury thread and/or thinning of the water film on the capillary wall. Consequently, this solution to the problem has not proven practical for the extended series of measurements needed for valid statistical analysis of stochastic data. We are still trying to overcome these experimental difficulties but time and resources are running out.

5. Inhibition

Condensed thymine monolayers inhibit many electrode reactions. With these monolayers we can vary the surface pressure (by varying the bulk thymine concentration) without changing the composition of the film or its charge density. The resulting inhibition behavior falls into two clearly distinct categories. In one, inhibition is independent of thymine concentration whereas, in the other, there is a quite pronounced effect, with more inhibition the higher the bulk thymine concentration.

This effect can be used to distinguish, experimentally, between electrode reactions involving electron tunneling, and those which require making or utilizing a hole in the condensed monolayer film. Examples of the latter would be reactions leading to metal deposition or dissolution, and also those involving adsorbed reagents, intermediates and/or products. These observations have been described in a manuscript which is in press [8], see appendix 2.

6. Related theoretical studies

We have developed a simple method to analyze the current-time transients resulting from voltage-step measurements on faradaic processes, such as used in our inhibition studies. A short note outlining our method has been published [9].

7. Related experimental studies

There are two different classes of compounds which form condensed films at the mercury-water interface. The most widely studied films have been formed from neutral species, such as thymine. Much less is known about salts forming similar films. We have therefore studied the adsorption of tetraphenylphosphonium chloride, using our maximum bubble pressure instrument. Our results illustrate the ambiguities involved in the analysis of simultaneous adsorption of anions and cations; they have been published [10]. A related short note describing the inhibition of a number of electrode reactions by tetraphenylphosphoniumchloride films has been submitted [11], see appendix 3.

In our attempts to find a better experimental system for nucleation studies, we have found examples in which diffusion-controlled adsorption can be described quantitatively. A short note describing these observations and their interpretation is in press [12], see appendix 4. We have also discovered examples of phase transformations following diffusion-controlled adsorption, specifically with tetrabutylammonium salts; a short paper describing these novel observations has been submitted [13], see appendix 5. Similar results have also been obtained with tetraphenylphosphonium and tetraphenylarsonium adsorption, but these data are still too fragmentary to warrant publication. We will complete this work provided we can weather the present financial difficulties. Finally, Dr. Lubomir Pospíšil from the Heyrovský Institute in Prague has, during a six-months stay in our lab, observed a number of film-forming systems which involve tris-

bipyridyl complexes of cobalt, nickel and iron, and has made a number of interesting observations on condensed films made with lipids. The latter measurements have subsequently been extended by Mr. Kontoyannis, who was able to demonstrate that prior heating of the lipid solutions (often used in order to facilitate their dissolution) causes an apparently irreversible, permanent change in the adsorption behavior of these lipids. These very recent results, which can be correlated with similar crystallographic observations on lamellar lipid phases [14], will soon be submitted for publication.

8. Didactic activities

In a somewhat unrelated effort, a manuscript on least-squares analysis was prepared for publication in the Journal of Chemical Education [15]. It will be published shortly, and is attached as appendix 6.

9. Bioelectrochemical observations

Our interest in stochastics and in the observation of single molecular events [16] led us to a study of biological systems which may exhibit similar phenomena. An extensive survey of the literature indicated that the so-called opioid receptor might be a good candidate. The existence of opioid receptors had been established in the early seventies; they are proteins embedded in neuronal membranes, on which opium, morphine, heroin, demerol and similar drugs act and cause pain suppression, euphoria and addiction. Shortly after the discovery of these receptors, several peptides were discovered which are the natural neurotransmitters

associated with them; the opiates apparently interact with the receptor in a similar way. The importance of these receptors in understanding the mechanisms of both pain suppression and drug addiction is obvious; our interest has primarily been focused on establishing whether or not these are electrochemical devices.

We have been able to solubilize a protein fraction from bovine brain which is enriched in these receptors. Using this partially purified fraction, we have succeeded in incorporating the receptors in an artificial lipid bilayer. In the presence of an applied voltage, and after addition of opiates or opioid peptides, these receptors make the membrane conducting. The conductance is abolished by known opioid antagonists such as naloxone, by sulfhydryl-alkylating agents such as N-ethylmaleimide, and by general proteases such as trypsin. These observations establish that, indeed, opium-like drugs act through an electrochemical mechanism, similar to the action of the neurotransmitter acetylcholine on its receptor. A short, preliminary note presenting these results has been published [17]. More recently we have been able to observe the opening and closing of single opioid receptor channels. These results will be communicated shortly.

10. Summary

During the two-year period covered in this report, our research effort has been most successful, as can be seen from the number of papers published and submitted; as indicated, a number of additional papers still remain to be written. Several of these papers and submitted manuscripts break new ground. The papers on

thymine, taken together, provide what we believe to be a uniquely thorough and comprehensive account of the thermodynamics and kinetics of film formation, a subject of considerable practical importance in corrosion protection. These papers include a number of novel ideas and new experimental approaches. Our work on opioid receptors, though somewhat outside the purview of the grant and the mainstream of electrochemical practice, is perhaps even more important; an improved understanding the mechanism of opiate action may also be of direct relevance to the armed forces.

It is ironic that, just as our research program is generating abundant and important results, a change of direction in AFOSR forces its termination. I am very grateful, however, for the years of generous support by AFOSR for our research effort.

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2. Condensed thymine films at the mercury-water interface II: Effects on electrode kinetics, R. Srinivasan & R. de Levie, J. Electroanal. Chem., in press [8].
3. Selective inhibition by tetraphenylphosphonium chloride, R. Srinivasan & R. de Levie, J. Electroanal. Chem., submitted [11].
4. On diffusion-controlled film formation and dissolution, R. Sridharan & R. de Levie, J. Electroanal. Chem., in press [12].
5. Direct evidence for interfacial condensation in the adsorption of tetrabutylammonium ions, R. Srinivasan & R. de Levie, J. Electroanal. Chem., submitted [13].
6. When, why and how to use weighted least squares, R. de Levie, J. Chem. Educ., in press [15].

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3. Adsorption of tetraphenylphosphonium chloride at the mercury-water interface, M. H. Saffarian & R. de Levie, J. Electroanal. Chem. 189 (1985) 325-337.
4. Electrochemical response of partially purified opioid receptors, J. W. Smuda & R. de Levie, J. Electroanal. Chem. 196 (1985) 443-446.

13. Manuscripts in preparation

1. Condensed thymine films at the mercury-water interface III: Thermodynamic studies, H. M. Saffarian, R. Sridharan & R. de Levie.
2. Condensed thymine films at the mercury-water interface IV: Nucleation and growth, R. Sridharan & R. de Levie.
3. On condensed lipid films at the mercury-solution interface, L. Pospíšil, C. Kontoyannis & R. de Levie.
4. Single-channel observations on the mu-opioid receptor, J. W. Smuda & R. de Levie.

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